

Ferric Oxyhydroxide Microparticles in Water

by Donald O. Whittemore* and Donald Langmuir†

Mineralogy and specific surface area are major controls on the stabilities of ferric oxyhydroxide microparticles in natural waters. The thermodynamic stabilities of ferric oxyhydroxides, as described by the activity product in solution $pK = -\log [Fe^{3+}][OH^-]^3$ range from $pK = 37.1$ for freshly precipitated amorphous oxyhydroxide to $pK = 44.2$ for well crystallized goethite. The sizes of suspended oxyhydroxide particles in natural waters range from less than $0.01 \mu m$ to greater than $5 \mu m$. Oxyhydroxides precipitated in the laboratory from solutions simulating high-iron natural waters are needlelike or lathlike in shape and have mean thicknesses as small as 60 \AA . Large specific surface areas resulting from the small sizes of ferric oxyhydroxide particles cause increased solubilities and thus decreased pK values. Specific surface areas of $40-170 \text{ m}^2/\text{g}$ determined for laboratory precipitates gave computed decreases in pK of 0.4 to 1.6 units.

Natural waters relatively high in dissolved iron ($>0.3 \text{ ppm}$) can occur in reducing environments such as certain ground waters, lake bottoms, and flooded soils, and in oxidizing conditions at low pH, such as acid mine drainage. When the dissolved ferrous iron is oxidized and hydrolyzed, ferric oxyhydroxides form. Naturally occurring ferric oxyhydroxides are listed in Table 1; of these, x-ray amorphous material and goethite are most commonly precipitated in surface and ground waters.

Table 1. Naturally occurring ferric oxyhydroxides.

Ferric oxyhydroxide	Ideal formula
Amorphous	indefinite
Goethite	$\alpha\text{-FeOOH}$
Lepidocrocite	$\gamma\text{-FeOOH}$
Akaganeite	$\beta\text{-FeOOH}$
Hematite	$\alpha\text{-Fe}_2\text{O}_3$
Maghemite	$\gamma\text{-Fe}_2\text{O}_3$

Concentrations of suspended ferric oxyhydroxides in New Jersey ground waters have been determined by subtracting the measured

concentration of dissolved ferrous iron from that of the total iron, and range from 0.002 to 1.0 ppm iron (1). The sizes of these suspended particles range from less than $0.01 \mu m$ to greater than $5 \mu m$ and average $1-2 \mu m$, as shown by filtration studies (2). Laboratory precipitation studies of ferric oxyhydroxides were conducted by using ferrous or ferric solutions which were prepared to simulate acid coal mine drainage. The procedure involved the addition of NaOH , Ca(OH)_2 , and NaHCO_3 to solutions 10^{-4} to $10^{-2} M$ in dissolved ferrous or ferric iron at 25°C . Mineralogy, relative amounts of phases, and mean particle thicknesses of the precipitates were determined by x-ray diffraction line positions, area ratios, and broadening, respectively. Acicular and rodlike goethite crystals were elongated in the $[001]$ or c -axis direction, while bladed lepidocrocite crystals were flattened on $\{010\}$. Precipitates prepared for x-ray diffraction analysis were allowed to orient by settling out of a dispersion on a glass slide. Thus, x-ray diffraction mean thicknesses were for the $[110]$ and $[010]$ directions for goethite and lepidocrocite, respectively. Particle morphology, widths, and lengths were determined by transmission electron microscopy. Particles were allowed to orient by drying a drop of dispersion on a collodion-covered grid.

*Department of Geology, Kansas State University, Manhattan, Kansas 66506.

†Department of Geosciences, The Pennsylvania State University Park, Pennsylvania 16802.

Average widths of goethite needles measured on electron micrographs were similar to their x-ray diffraction thicknesses (1,3). An example of ferric oxyhydroxide precipitate from a ferric sulfate solution aged for 80 days is shown in Figure 1. X-ray diffraction analysis indicated that it contained poorly crystalline goethite with a mean thickness of 60 Å. Electron

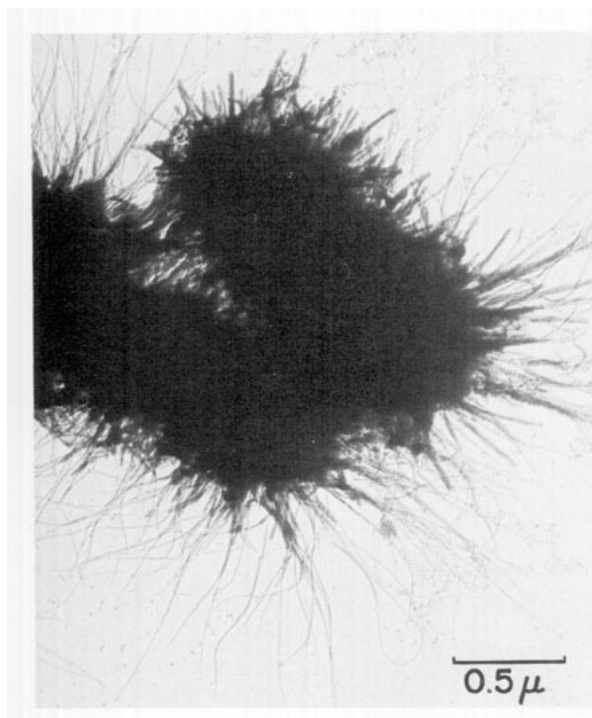


FIGURE 1. Electron micrograph of ferric oxyhydroxides precipitated from ferric sulfate solution.

micrographs of oxyhydroxides precipitated from ferrous sulfate solutions aged for 302, 298, and 100 days are shown in Figures 2, 3, and 4, respectively. The needlelike particles in Figure 2 are aggregations of goethite and lepidocrocite crystals with x-ray diffraction thicknesses of about 100 and 200 Å, respectively. Figure 3 shows a mixture of lathlike lepidocrocite crystals and smaller goethite needles with mean thicknesses of approximately 90 and 60 Å, respectively. In Figure x-ray diffraction mean thicknesses are about 130 Å for lepidocrocite laths and 60 Å for narrow prisms and needles of goethite.

The thermodynamic stabilities of the ferric oxyhydroxide can be described by the activity product in solution (1):

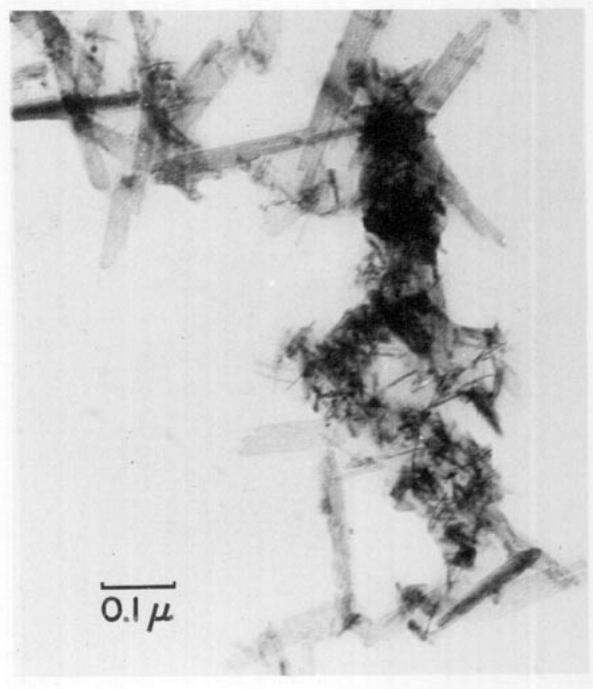
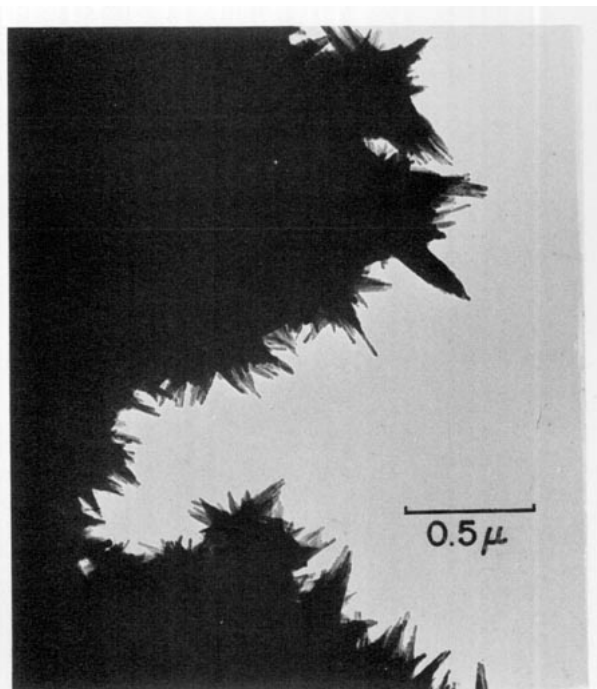


FIGURE 3. Electron micrograph of lathlike lepidocrocite crystals and smaller crystals goethite crystals precipitated from ferrous sulfate solution. Aged for 298 days.

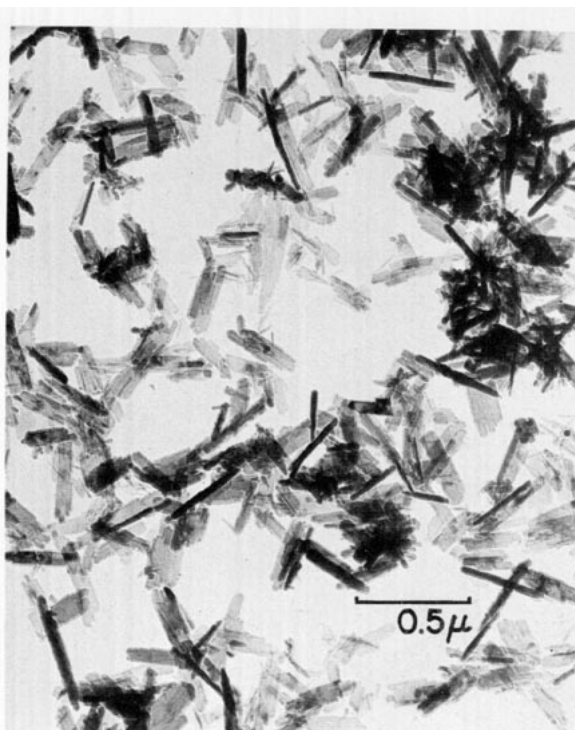


FIGURE 4. Electron micrograph of lathlike lepidocrocite crystals and smaller needlelike goethite crystals precipitated from ferrous sulfate solution. Aged for 100 days.

$$pK = -\log [Fe^{3+}][OH^-]^3$$

pK values range from 37.1 for freshly precipitated amorphous oxyhydroxide to 44.2 for coarsely crystalline goethite (Table 2). This means that at the same Eh (oxidation potential) and pH conditions, approximately seven orders of magnitude more dissolved iron can exist in waters in equilibrium with fresh, amorphous material than in equilibrium with well-crystallized goethite. Apparent stability values of naturally occurring oxyhydroxides calculated from Fe(II), Eh, and pH measurements in several types of high iron ground and surface waters ranged between the limits 37 to 44.

Table 2. pK Values of ferric oxyhydroxides.

Ferric oxyhydroxide	pK
Amorphous	37.1 ± 0.1
Lepidocrocite	41 ± 2
Hematite	44.0 ± 0.4
Goethite	44.2 ± 0.4

Surface area effects are a major control on the stabilities of ferric oxyhydroxide microparticles. Larger specific surface areas resulting from smaller particle sizes cause increased solubilities and thus, decreased pK values. Figure 5 illustrates this change for the pK of goethite and hematite for surface energies of 600 and 770 ergs/cm², respectively. Surface

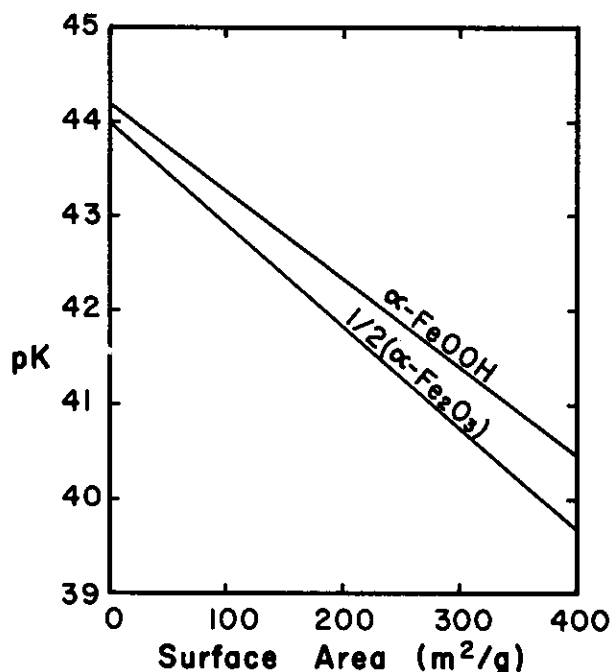


FIGURE 5. Effect of specific surface area on pK of goethite ($\alpha\text{-FeOOH}$) and hematite ($1/2 \alpha\text{-Fe}_2\text{O}_3$).

areas were calculated from the mean particle dimensions measured by x-ray diffraction line broadening and electron microscopy. Lath or cylindrical shapes were assumed for the calculation depending on the particle morphology.

Surface areas were also measured for a few samples by negative adsorption in solution according to the procedure of van den Hul and Lyklema (4). Hydrogen ions were the potential-determining ions, being adsorbed at acidic pH on the ferric oxyhydroxide surface to produce a positive charge. Added Mg^{2+} ions were expelled (negatively adsorbed) from the positive oxyhydroxide surfaces. The resulting increase in the Mg^{2+} concentration, which varies as a function of the total surface area, was measured and used in surface area calculations.

Specific surface areas of crystalline oxyhydroxide precipitates calculated from the geometric and negative adsorption measurements ranged from 40 to 170 m²/g. These gave computed decreases in p*K* of 0.4 to 1.6 units.

In conclusion, the mineralogy and the specific surface area are probably the major controls on the stabilities of ferric oxyhydroxides in natural waters. It is suggested that surface area measurements could also provide important information, in addition to the particular mineral used and its particle size, in investigations of the biological effects of asbestos particles.

REFERENCES

1. Langmuir, D., and Whittemore, D. O. Variations in the stability of precipitated ferric oxyhydroxides. In: *Non-equilibrium Systems in Natural Water Chemistry*, (Advan. Chem. Ser. 106:), American Chemical Society, Washington, D.C., 1971, p. 209.
2. Langmuir, D. Geochemistry of iron in a coastal plain ground water of the Camden, New Jersey, area. U. S. Geol. Survey Prof. Paper 650-C, C224-C235 (1969).
3. Whittemore, D. O. The chemistry and mineralogy of ferric oxyhydroxides precipitated in sulfate solutions, Ph.D., Thesis, Penn. State Univ., University Park, Pa. 1973.
4. van den Hul, H. J., and Lyklema, J. Determination of specific surface areas of dispersed materials. Comparison of the negative adsorption method with some other methods. *J. Amer. Chem. Soc.* 90: 3010 (1968).